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STUDIES IN THE FORMATION OF SILICATES AT STEAM TEMPERATURES

BY

T. R. ERNEST, A. B., 1907

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

T. R. Ernest, A. B., 1907.

ENTITLED Studies in the Formation of Silicates at Steam Temperatures.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Master of Arts

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INTRODUCTION.

The immense deposits of fine-grained silica found in Southern Illinois have been the object of many inquiries at the State University, as to some adequate use for the material, and have furnished very largely the inspiration for this work. When a new material is found it is turned over to the chemist for examination, and he is expected to answer the question, "What is it good for?" It is the same when a commodity, already having a limited use, is suddenly made available in large quantities, either through the opening of new sources of supply, or a reduction in the cost of production.

Amorphous silica has had an application in the arts for many years. It has been used as a scouring material, and in the manufacture of various scouring soaps and other commodities of a similar nature. The present uses for amorphous silica are, however, entirely out of proportion with the supply, and the material is clamoring for an application that will give it a satisfactory market.

These deposits are worked in several localities at present, and there are several mills engaged in preparing the material for market. This process includes rough crushing and careful sizing. Very little capital is, as yet, invested in this industry, and most of the work is done by hand. No new uses have been found for silica since the opening of these deposits, hence the effect of their discovery has been only

to overstock the market and cause a lowering in the price of silica.

Our knowledge of the geology of this region is still very limited. Mr. F. W. DeWolf visited it in the year 1906 in the interests of the State Geological Survey, making preliminary observations on the mode of occurrence, and collecting some representative samples. The material occurs, we are told, much as do clays. The veins vary in thickness from only a few,to six or eight feet, and crop out in many places on the hillsides. The report of this investigation may be found in the Year Book of the Survey for 1906 (Bulletin No. 4). Table No.1 is copied from this bulletin, and shows the results of chemical analysis of the samples. The analyses were made by Mr. L. C. Turnock under the direction of Professor Parr.

Table No. I

No.	Per cent SiO_2	Per cent $Fe_2O_3+Al_2O_3$	Loss on ignition
203	87.90	3.72	2.84
204	88.26	6.04	1.76
205	95.14	2.38	
206	90.24	5.88	
207	95.18	1.04	
208	90.04	2.36	
209	73.78	14.56	5.43
210	97.20	1.28	
211	95.78	1.80	
212	77.82	10.26	

Note: Iron and alumina were separated in No.209&212.

Acknowledgement is due Mr. C. F. Hagedorn '05 who in the fall of the year of his graduation began a similar line of research, getting far enough to make some brick such as were made in this investigation; and to Mr. C. H. Mc Clure who took up the work after him, making a few determinations of lime and silica. Both of these gentlemen were, however, called into other fields of activity and so were unable to carry the work very much beyond the beginning. Some of the samples made by these gentlemen were used by Mr. H. B.Fox in tests on sand-lime brick to be referred to in another connection. All the work on this material done at the University has been in the department of Applied Chemistry of which Professor Parr is head.

The object of this investigation has been three-fold viz:-

1. To study thoroughly the sand-lime brick process with a view to finding an application for Illinois silica.

2. To study the compound formed by the action of high pressure steam on mixtures of lime and silica, from both the chemical and physical standpoint.

3. Uses for Illinois silica, including both a review of the literature and experiments.

PART FIRST

Unlike clay brick sand-lime can boast of no proud record antedating the dawn of history. The modern sand-lime brick process is new, and owes its possibility to the excellent properties of modern steels. Brick have been made, however, from these materials for many years. The first brick made exclusively from sand and lime were what are now more properly termed mortar brick, and were in fact only hardened mortar. In many parts of the Old World this kind of brick was made, especially where sand and lime were plentiful, and clays were not available. A locality such as this is to be found surrounding the little town of Potsdam, Germany. Here the attention of Dr. Michaelis was first called to this peculiar kind of brick. He then went to work to find some way of shortening the process of manufacture, or rather the hardening process, and about the year 1880 took out patents covering the steam hardening process which is in use at this time.

The industry did not develope in Germany until about the time of the expiration of Dr. Michaelis' patents. In the year 1896 there were in this country five factories using the new process, and from that time on till now the industry has grown rapidly. America was somewhat slower in establishing the industry, the first factory being opened about the year 1901. Here as in Germany growth has been rapid from the beginning. The following table from an advance chapter from Mineral Resources of the United States for 1906 will give a fair idea of the growth of the industry since 1903.(In the year 1901 there were in this country two factories.)

Table No. 2.

Year	Number of plants	Value of product
1903	16	155,040.00
1904	57	463,128.00
1905	84	973,064.00
1906	87	1170,000.00
1907		1,225,[illegible]
1908	87	98[illegible],186.00

Brick of three distinct types are now made from exactly the same materials,(lime and sand) and go indiscriminately under the same name. The first two have little commercial importance and will be passed over hurridly. The third,however, is our modern process and will be dwelt upon much more at length.

MORTAR BRICK

Mortar brick is the oldest of all brick made from sand and lime, as has already been intimated. These brick are made by mixing the thoroughly slaked lime with sand just as in making mortar, moulding same into blocks, somewhat after the fashion of making clay bricks by the soft mud process, and allowing them to dry and harden in the atmosphere. The reaction that takes place affects only the lime changing it into the hard insoluble carbonate thus:-

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

The bond is,in this case,evidently a mechanical one as there is no chemical union between the sand and lime. The brick is essentially a network of calcium carbonate in which grains of sand are embedded. The necessity of using a relatively

large quantity of lime will be apparent as it must surround almost completely the sand grains if a good bond is to be obtained.

Reasonably good brick are made by this method if the mortar is properly prepared and time enough is allowed for hardening. The great disadvantage of this process is that too much time is required for the hardening process. This necessitates the employment of large amounts of capital and hence increases the cost of production. Again the hardening is from without toward the center so that the external appearance gives little idea as to the nature of the interior.

SAND,LIME BRICK IN WHICH THE BOND IS BOTH CARBONATE AND SILICATE OF CALCIUM.

Brick of this type are made by mixing and moulding the lime and sand just as in the former case. The hardening process differs,however, in that the brick are subjected to both moist air and carbon di-oxide in an enclosed chamber. Some artificial heat is also generally supplied. This may come either from waste furnace gases or exhaust steam. The carbonic acid usually comes from lime kilns or furnace gases. Much less time is required here than in the former case since we have two reactions going on together,viz:-

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O .$$

$$xCa(OH)_2 + SiO_2 + yH_2O = xCaO \cdot SiO_2 \cdot yH_2O .$$

The product is of a somewhat higher order than that by the former process,the bond being both mechanical and chemical, though the principal advantage of this over the former, is the shortening of the time required for hardening.

SAND-LIME BRICK PROPER

The term sand-lime brick as properly used at the present time includes only those brick made from sand and lime in which the bond is a hydrous calcium silicate produced by the action of high pressure steam. This is the only class having any commercial importance to-day; the one that is threatening to take the market from clay brick in many localities favorable to their manufacture. The subsequent paragraphs of this work will be devoted to a review of the literature on this subject.

All true sand-lime brick are made in the same general way. As has been said before, the ground patents were taken out by Michaelis and are no longer active. The finished product is essentially a mass of sand cemented together by a hydrous calcium silicate. The reaction by which the bond is formed does not run to completion, hence there is always some free lime in the brick when first finished. On being exposed to the air for a time this passes over into the carbonate. The process of manufacture is briefly as set forth in the following paragraph.

Numerous patents have been issued, both in this country and abroad, on the various processes in use for preparing the material for the press, and on many other details of the process, but whatever particular method of procedure may be adopted there will be the following steps:

1. Slaking the lime
2. Mixing it with the sand
3. Adding the right quantity of water
4. Pressing into bricks

5. Hardening, or steaming.

In describing the various processes it has seemed best to follow the material through the factory mentioning the different ways of carrying out each operation. Should the reader be interested in any of the particular processes, references may be found at the end of this work. Assuming that the raw materials are lime and dry sand, the first step in the process of manufacture is the preparation of the lime for the mixture. In most cases this is done by slaking. For slaking the lime there are, what are known as the wet, dry, acid, and steam slaking processes, with their modifications.

THE PREPARATION OF THE LIME

In the wet process the lime is brought into contact with enough water to thoroughly slake and leave it as a thick paste, in which form it may be stored for a time. It is claimed by the advocates of this method that none of the lime will escape hydration, and that the volume of the resulting hydrate is about twice as great as when a large excess of water is used, or about 30% greater than when the hydrate is the result of air slaking. This treatment, they say, gives it a greater plasticity, and makes it easier to coat the grains of sand in the subsequent mixing process.

In the dry process just enough water is added to combine chemically with the lime, leaving a dry powder as the product. In this process, where a calculated quantity of water is added and where much of it is lost by evaporation, the likelihood of some of the lime escaping thorough hydration will be apparent. The volume of the hydrate is not so

great as when the wet process is used, but the dry hydrate is much more easily mixed with the sand and so less power is consumed in the mixing.

In the acid slaking process five to ten per cent of a solution of hydrochloric acid is added after slaking has begun. The acid, of course, combines with the lime forming calcium chloride and water. The advocates of this method claim that this treatment shortens the time required in the hardening cylinder. The calcium chloride is supposed to act catalytically promoting the combination of the lime and sand according to the following reactions:-

$$CaCl_2 + SiO_2 + H_2O = CaSiO_3 + 2HCl$$

$$Ca(OH)_2 + 2HCl = CaCl_2 + H_2O.$$

It will be evident that either hydrochloric acid, calcium chloride, or both will be the final product of the reaction. The effect of free hydrochloric acid on the steel hardening cylinder will be to shorten its life very materially, unless it be lined with some acid proof material, which would add very materially to its cost. Should calcium chloride remain in the finished brick, it would be noticed later as an efflorescence on the its surface. There can hardly be a doubt that the disadvantages of this method more than offset the small benefit to be derived from the shorter time required for hardening.

The steam slaking process makes use of a closed cylinder mounted on trunnions so that it can be rotated. A charge of the lime to be slaked is first dumped into the cylinder. It is then closed steam tight, and enough water pumped in to

to slake it. The heat of hydration generates considerable steam pressure, which aids very materially in effecting complete hydration. The cylinder is rotated during the process, which lasts for about half an hour. This method gives a dry, and thoroughly slaked lime. Its principal disadvantage lies in the fact that expensive machinery is employed, and that the process is intermittent.

Essentially the same effect is obtained in many plants by providing trucks, having iron boxes beneath the platform, for holding lime. These boxes are filled with the lime to be slaked. The trucks are then loaded with the green brick and run into the hardening cylinder. By this method the heat of hydration of the lime is used in heating up the cylinders and the raw brick, thus saving considerable heat energy and shortening the time required for hardening. The method gives a good lime that is practically dry.

Another method used for slaking lime in some of the European countries combines the wet and steam slaking processes. A long, steel tube mounted as is the rotary kiln, is fed at the upper end with quick lime and water, while superheated steam is blown in at the lower end. By this process the lime is slaked with an excess of water in the upper end of the cylinder, while in the lower end it is thoroughly dried. This also gives a good hydrate.

There is one process in which the lime is not slaked before mixing with the sand. Here the lime is first crushed and powdered, then mixed with the sand, and water added. This proceedure combines two steps imto one. The manner of adding

the water is about the same as in the other processes.

PREPARING THE MIXTURE FOR THE PRESS

For blending the lime and sand two radically different processes are employed,viz; the wet and the dry. The one to be employed will depend somewhat on the process employed in slaking the lime. If this be done wet,the wet blending process will be most suited, if dry the dry blending process. Opinions differ as to the relative merits the two methods. Less power is required in the dry process, and a more perfect mixture can be prepared in a shorter time, than by the wet process. On the other hand if the sand be wet when it comes into the factory, the wet process has a decided advantage in that the drying operation is eliminated. The local conditions must determine very largely what process is to be used.

In the wet process enough water is added so that the materials can be mixed in a pug mill or similar machine.The mixture may then be stored in a silo for a time before going to the press.

In the dry process the sand and lime are brought together dry and thoroughly blended. Water is then added until the material will cling together when pressed in the hand. It is then in most cases put into a silo for awhile. This allows the water to distribute itself uniformly throughout the mass.

The practice of grinding a part of the sand is becoming pretty general, although there are still many manufacturers who do not go to the trouble to do this. The desirability of having some fine sand present will be apparent to any one

at all familiar with chemical reactions.

PRESSING

Little need be said under this heading except that an exceptionally strong press is required. In Vol. V of the Transactions of the American Ceramic Society (1903), may be found a report of some work on this subject by Mr. S. V.Peppel, of Columbus, Ohio.

HARDENING

The brick may be hardened either by low pressures for a long time or by high pressures for a short time.The processes are equally efficient so far as the quality of the brick is concerned. The following table, showing the relative effects of high and low pressures, is from the work of Peppel referred to above. T

Table No. 3.

Hours in	A		B		C		D		E	
Steam	CS	TS	CS	TS	CS	TS	CS	TS	CS	TS
	Steam Pressure, 150 Pounds									
4	7896	544	5303	392	5282	591	4514	470	4441	330
6	7994	390	5045	190	....	...	....	...	....	...
8	7404	509	4957	262	6170	632	4249	430	4491	337
10	7767	464	4902	284	....	...	....	...	....	...
12	7514	337	5064	250	6165	556	4543	434	4924	349
14	7894	380	5849	329	....	...	....	...	....	...
	Steam Pressure, 120 Pounds									
4	6989	...	5989	...	5403	...	4300	...	5760	...
6	7063	...	6495	...	....	...	....	...	....	...
8	8545	...	6038	...	5868	...	5142	...	6718	...
	Steam Pressure, 100 Pounds									
4	6385	...	5921	...	4280	...	4048	...	4588	...
8	7566	...	6507	...	5564	...	4456	...	6544	...
12	7494	...	5753	...	....	...	....	...	....	...

Note: "CS" and"TS" refer to"crushing strength" and "tensile strength" respectively.

We learn from this work that 150 pounds for four hours , 120 for eight, or 100 for twelve hours, will suffice to bring about the desired reaction.

THE PURITY OF THE RAW MATERIALS

Regarding the quality of the sand and lime to be used in this new building material, it may be said that a high degree of purity in both is necessary if the best quality of brick is to be produced. A fairly good product may, however, be made from inferior raw materials by suitably modifying the process.

The sand should not be too coarse grained, nor should the size of grain be too nearly uniform. It is also desirable to have a sharp grained rather than a round grained sand. The sharp corners give a better chance for the lime to attack the sand, and at the same time help to hold the brick together better while in the green condition. Experiments by the writer confirm these statements. Brick were made under exactly the same conditions, with the exception that in one a round grained sand was used while in the other a sharp grained sand of the same size was employed. The size of the sand was between twenty and thirty mesh. When the round grained sand was used with no amorphous silica the bricks would not stand up in the hardening cylinder. Table No. 4 shows the average of a number of tests on brick made with these sands, ten per cent of slaked lime, and ten per cent of amorphous silica.

Table No. 4.

Sample	Absorption	Crushing S'th
Round Sand	10.6	1290 lbs.
Sharp Sand	10.5	4500 lbs.

In the Thon Industry Zeitung Vol. 24 and 25, and pages 1703, and 762 respectively, we have the results of some work by Prof. M. Gasenopp of the technical laboratory of the Polytechnic Institute at Rega, wherein he shows the desirability of using some fine-grained sand. He ran parallel experiments using in one a sand having a diameter of grain .6 to 1 mm., and in the other a fine sand of from .2 to .3 mm. diameter. He used mixtures containing both 10 and 20 per cent of lime, and employed dolomitic as well as high calcium limes. The results of his work are shown in the following tables.

Table No. 5.

Percentage of Caustic Filler	Pressure of Steam #	Percentage, Soluble Silica Found		
		Caustic Filler £	Using Coarse Sand	Using Fine Sand
10	5	Calcium	0.43	3.06
		White	0.75	1.98
	10	Calcium	3.33	7.58
		White	3.14	6.29
20	5	Calcium	0.59	3.41
		White	0.65	....
	10	Calcium	2.75	11.14
		White	1.69	7.03

The steam pressure is expressed here in atmospheres per square inch.

£ The terms "white" and "calcium" refer to dolomitic and high calcium limes respectively.

Reference to these tables will show clearly the greater reactivity of the fine sand under all conditions, and hence the desirability of grinding a part of this constituent or in some way introducing fine grained silica.

Table No. 6. #

No.	Steam Pressure in Atmosph'res	Combined Water	Soluble SiO_2	Mixture
1	5	0.88	0.43	(90 parts coarse sand (10 " lime
2	10	[illegible].96	3.33	Same as No. 1
3	5	2.78	0.59	(80 parts coarse sand (20 " lime
4	10	4.60	2.75	Same as No.3
5	5	1.79	3.06	(90 parts fine sand (10 " lime
6	10	2.55	7.58	Same as No.5
7	5	3.90	3.41	(80 parts fine sand (20 " lime
8	10	3.59	11.14	Same as No.7

A comparison of samples No. 1 and 5, 2 and 6, 3 and 7, etc. will show the tremendous effect of the fineness of grain upon the extent of chemical reaction. The following table from the work of Peppel shows the effect of the addition of fine sand on the strength of the brick.

Table No. 7.

No.	Composition		Crushing St'gth	Tensile St'gth
	Parts Course	Parts Fine	Pounds sq. in.	Pounds sq. in.
77	8	2	3114	131
79	4	2	2955	144
84	3	2	2461	224

Mr.Peppel says concerning this work: "From the foregoing I would conclude that in order to maintain thebest conditions, and using a sand all of which would be retained on a 40 mesh screen, we should have to grind one-fourth of the sand so that at least one-half of it would pass a 150 mesh screen.If, however, we had a sand with a good assortment of sizes from

coarse to fine, we ought to have sand finer than 150 mesh at least equal in amount to the weight of the lime to be added."

"The fine sand not only fills the spaces between the c coarser particles, but assists in the even distribution of the lime, and very much accelerates the chemical reaction so necessary to strength."

In the same paper Mr. Peppel discusses also the allowable impurities in sand and lime to be used in sand-lime brick. The ordinary impurities found in sand are clay, composed largely of kaolin, mica, and feldspar, with a varying amount of iron oxide. Mr. Peppel's first work was to show the effect of kaolin. The results of his experiments shown in the following tables are taken from his paper as published in the Transactions of the American Ceramic Society.

Table No. 8.

Data:- Moulding Pressure- 10000 lbs. sq. in.

Steam '' 150 '' '' ''

Temperature of hardening cylinder-- 185° C.

Time exposed to steam-- 10 hours.

Composition of Mixtures				Per Cent Qu'ck l'me	When Tested At once		After aging		After freezing		
No.	S	F	K	PL	D	CS	TS	CS	TS	CS	TS	A
85	4	1	2.5	....	5	2766	338	2449	194	2917	219	8.3
86	4	1	5.0	....	5	2500	210	2376	277	2481	181	8.0
87	4	1	10.0	....	5	1943	184	1687	157	1910	121	8.5
88	4	1	20.0	....	5	1705	162	1325	138	1477	93	9.0

The terms "CS" and "TS" are used in the same sense as in "3."

"S", "F", and "K" refer respectively to the number of parts of coarse sand, fine sand, and kaolin; "PL" and "D" have reference to the number of per cent of pure and dolomitic lime used, and "A" is the per cent of absorption.

Table No. 8. (Continued)

93	4	1	2.5	5	.	3835	351	3955	365	4502	352	8.6
94	4	1	5.0	5	.	3340	295	3342	175	3887	269	8.6

This table shows the effect of kaolin on the strength of the brick where both pure and dolomitic limes are used. We learn from these figures that kaolin has a very deliterious effect on the strength of the brick when present in considerable quantity. Mr. Peppel studied the effect of this impurity under many conditions,and says regarding the work:-

"Reviewing the facts expressed in tables II, III, and IV, (No. 8. in this work) where the brick are made under a pressure of 10000 pounds per square inch, we observe that with each addition of kaolin there is a marked decrease in both tensile and crushing strength, this being most marked in table III, where in test 83 the proportion of flint was large and in test 89, where all of this flint was replaced by kaolin. Also we observe that the decrease in crushing strength is at least one-third with the addition of 20 per cent kaolin."

The results of the experiments on sand carrying feldspar do not have the same deleterious effects on the strength of the brick as do those with the kaolin; but if lime reacts with feldspar it is safe to conclude that the finished brick will be afflicted with the troublesome property of efflorescence, owing to the liberation of alkaline salts.

The effect of iron was found to have no other effect than to change the color slightly if present in moderate quantities such as would be likely to be found in sands.

To sum up the conclusions, then, in regard to the sand we have the following:-

1. A part of the sand should be fine-grained.

2. A sharp-grained sand is to be preferred.

3. It should carry not more than 10 per cent of clay for economic production.

4. Moderate amounts of iron and feldspar do not affect the strength of the brick very materially, but may affect the appearance.

For our knowledge regarding the effect of various grades of lime we are again indebted to Mr. Peppel. He first studied the effect of increasing the lime content, keeping other conditions the same. The results of this series of experiments is shown in the following table.

Table No. 9.

Composition of Mixtures							When Tested				
			%CaO		At once		After agging		After freezing		
No.	S	F	PL	D	CS	TS	CS	TS	CS	TS	A
83	3	2	..	5	3697	427	....	...	3812	...	8.06
90	3	2	..	10	5607	503	5843	446	7525	417	9.87
84	3	2	5	..	2636	194	....	...	....	...	10.25
97	3	2	40	..	7018	541	7153	622	7995	516	12.13

Symbols used to head columns in this table have the same meaning as in table No. 8.

It will be seen that while an increase in both tensile

and crushing strength is observed with each increase of lime, the increase in strength is in no way proportional to the increase in lime content, and that the divergency becomes more marked as the latter increases. The conclusion is that the present practice is about right in regard to the quantity of lime to be used.

To ascertain the relative values of pure and dolomitic limes Mr. Peppel ran the experiments shown in the following table.

Table No. 10.

Composition of Mixture					When Tested				
			%CaO		At once		After freezing		
No.	S	F	PL	D	CS	TS	CS	TS	A
A	2	1	10	..	7745	437	9007	371	8.62
B	2	1	..	10	5187	286	5853	314	9.11

#"A"and"B" are the average results obtained from a number of samples. The symbols used in the headings have the same meaning as in previous tables.

A glance at this table will show that the high calcium limes are in every respect the best. Just why this is true would be difficult to say as magnesium oxide combines with silica almost as readily as does calcium oxide. The only explaination available at the present time is that the magnesium silicate is not so strong as the calcium silicate.

The general conclusion with regard to the lime seems tobe that either a fat or a white lime can be used,if properly handled, and reasonably good brick obtained. The advantages however, are all in favor of the high calcium limes. Impure

limestones require great care in burning, and this is especially true of dolomitic limes. If these be overburned the magnesium oxide will be converted into the crystalline form which slakes with extreme slowness. The same effect is observed when calcium oxide is heated to a high temperature, but this temperature is not easily reached in the case of high calcium limes. The impurity most disastrous to proper burning is clay. If clay be present in considerable quantity,a temperature slightly above that necessary to drive off the carbon di-oxide will cause a combination between the lime and the constituents of the clay. This compound will then act as a dilutant to the lime, cutting down very materially its efficiency in the sand-lime brick process. The effect of underburning is to leave some of the carbonate undecomposed which acts as a dilutant just as does the calcium silicate already referred to. This point must be closely watched in dolomitic limestones.

THE CHARACTER OF THE MATERIAL

The value of building brick depends primarily upon their strength, durability, appearance, and the uniformity of the product.

In appearance sand-lime brick are in a class by themselves. The color is usually a dull gray, but it is not in any way restricted to this hue, as any desired shade can be obtained by incorporating the proper coloring matter.in the raw mixture. The brick are uniform in every respect,and the edges are straight and sharp.

The strength of good sand-lime brick is entirely adequate to meet all the requirements for building purposes. The

strength of the best sand-lime brick falls short of that of the best clay brick, however, and even the average sand-lime brick will hardly compare with the average clay brick in this respect. But in this new material we have a much more nearly uniform product than we have in clay brick, and as the brick should be judged by the poorest that goes on the market, there can be no doubt that this brick will compare favorably with clay brick as found on the market.

Much work has been done along this line both in this country and abroad. The following tables were published in the Technograph(No. 19)by L. E. Kurfman '05, and represent his work on the transverse and crushing strength of this material.

Table No. 11.

Transverse Strength

Ref. No.	Private Mark	Kind of Brick	Modulus of Rupture, lb. per sq.in.	Number in Test	Result by
1	C	Sand-lime	509	15	Curfman
2	CS	"	766	3	"
3	U	"	420	10	"
4	S	"	607	22	"
5		Clay	1721	9	"
6		"	800		Baker #

Treatise on Masonry Construction, p. 13.

The results shown in this table do not appear very favorable to sand-lime brick, but it must be remembered that the industry was passing through the experimental stage in this country at the time that the samples tested here were made.

Table No. 12.

Crushing Strength

Ref. No.	Private Mark	Kind of Brick	Modulus of Rupture lbs. sq. in.	Number in Test	Result by
1	CS	Sand-lime	4344	12	Curfman
2	C	"	6123	3	"
3	U	"	2412	12	"
4	S	"	2244	13	"
5	"	"	7300		See note
6	"	"	952	15 cubes	"
7	"	"	2943	10	"
8	"	"	4470	1	"
7	"	"	3002	2	"
10	"	"	3147	1	"
11	"	"	3848	3	"
12	.	Clay	5690		Baker

Note: Numbers 5 to 10 were taken from the literature on the subject, from various sources. No. 6 is from the work of Mr. H. B. Fox formerly of this University. The results of this investigator all seem to be abnormally low, when compared with those of other investigators.

In its ability to withstand the disintegrating action of frost in this climate, is where we would expect to see sand-lime brick fail. The popular belief is that it will absorb a great deal of water, and that when wet the frost will easily tear it to pieces. Owing to this fact much work has been done to determine the effect of frost, and to get some idea as to the probable time that the brick may reasonably

be expected to withstand the action of the weather. The following table is taken from Vol. 25 of the Thon Ind. Zeit. 575.

Table No. 13

No.	Absorption Water absorbed by dry sample,%dry Wt.	Crushing Strength,in pounds per square-inch Soaked	Dry Brick	Frozen
1	12	1903	1704	2229
2	14	2073	2215	2300
3	9	3933	4189	4260
4	10.6	1846	1732	2187
5	..	....	3710	3238
6	..	....	850	1335
6a	..	....	1353	1747
7	18.3	1335	1193	1562

This table shows conclusively that the strength is not affected materially by freezing. In those cases where the strength shows an increase after freezing, it is very probable that this is due to the change of free lime to the carbonate by the action of carbonic acid dissolved in the water used in the experiment.

Fox, in his work on the relative values of sand-lime and clay brick, made abrasion tests in which he showed that, in this respect, sand-lime will not bear even a comparison with clay brick. This test, however, is hardly needed unless this material is to be used for street paving or in other places where it will be subjected to wear.

Numerous articles have appeared in the literature regarding the effect of fire on sand-lime brick. Most of these have been of a semi-popular nature, in which the writer has descri-

bed the brick after they have been subjected to the action of the fire of a burning building. It has been claimed that in fires where both sand-lime and clay brick have been subjected to the same conditions the former remained unaltered while the latter went to pieces.

We have also the work of Curfman on this subject in which he sent both sand-lime and clay bricks through the furnace of a boiler on the traveling grates of an automatic stoaker, and again where he heated both in a wood fire to a moderate temperature. His work showed that the bond is broken up by the action of heat so that the brick can be easily broken by a slight blow with a stick. No attempt was made to measure the temperatures in these experiments.

Peppel made fire tests also, his results agreeing with what has already been said,so far as low temperatures are concerned. But this investigator employed high temperatures also, and found that if the temperature runs high enough a very good brick is the result. He says, "The only change observable was that they were whiter, and had taken on a semi-vitreous lustre."

From these experiments and from the nature of this material, the effect of fire should be evident. Since it is essentially sand grains cemented together by an hydrous calcium silicate, it will be easy to see that a temperature high enough to drive off the combined water will result in the destruction of the bond. A higher temperature, however, will cause a recombination of the lime and silica, forming a new brick of the same size and shape as the first, but the new brick will not be a sand-lime brick. It will be more properly designated

silica brick, as the bond in this case is not an hydrous, but an igneous silicate. The temperature to which it is necessary to raise the heat will depend on the composition and physical properties of the brick.

The following table copied from Peppel's work (Trans. Am. Cer. Soc.) is intended to give an idea of the relative strengths of sand-lime brick and sandstone used for building purposes.

Table No. 14

	Natural Sandstone	Sand-lime Brick
Weight per cubic foot	137 lbs.	136 lbs.
Absorption	7.3%	8%
Crushing Strength	6535 lbs.	7745 lbs.
Coefficient of Elasticity	165440	600000

These figures will show that sand-lime brick compares very favorably with building sandstone in every respect.

EXPERIMENTAL WORK (PART TWO).

Test blocks were made of amorphous silica and lime, and of silica, lime, and sand, and these were tested by physical and chemical methods. The amorphous silica was from Southern Illinois. The lime was of a good commercial grade. The sand was of two kinds, a round grained one passing a 20 mesh screen and retained on a 30, and a sharp grained one of the same size. The lime was slaked with just enough water to hydrate it thoroughly, and was kept stored for some time before use. In every case the lime and silica, or lime, silica, and sand, were mixed and placed in a ball mill with a few flint pebbles, and rolled for about an hour so as to insure a thorough blending of the materials. Pressure was obtained from a testing machine of one hundred thousand pounds capacity. The steam heating was done in a small autoclave belonging to the department, capable of withstanding a pressure of 25 Kg. per sq. cm. Two moulds were employed, one was circular having a radius of one inch, the other rectangular with a cross section of approximately ten inches.

THE CHEMICAL WORK

The test blocks used in chemical analysis were made in two lots. In the first five were made, in which amorphous silica and lime were used in the proportion to form $CaSiO_3$. The pressures used will be shown later in table No. 15. The steaming was for eight hours at about 150 pounds per sq. in. Another series of blocks was made in which 40, 50, and 60 per cent of lime were employed, the remainder being amorphous silica. The work was carried out in substantially the same manner as in the first series.

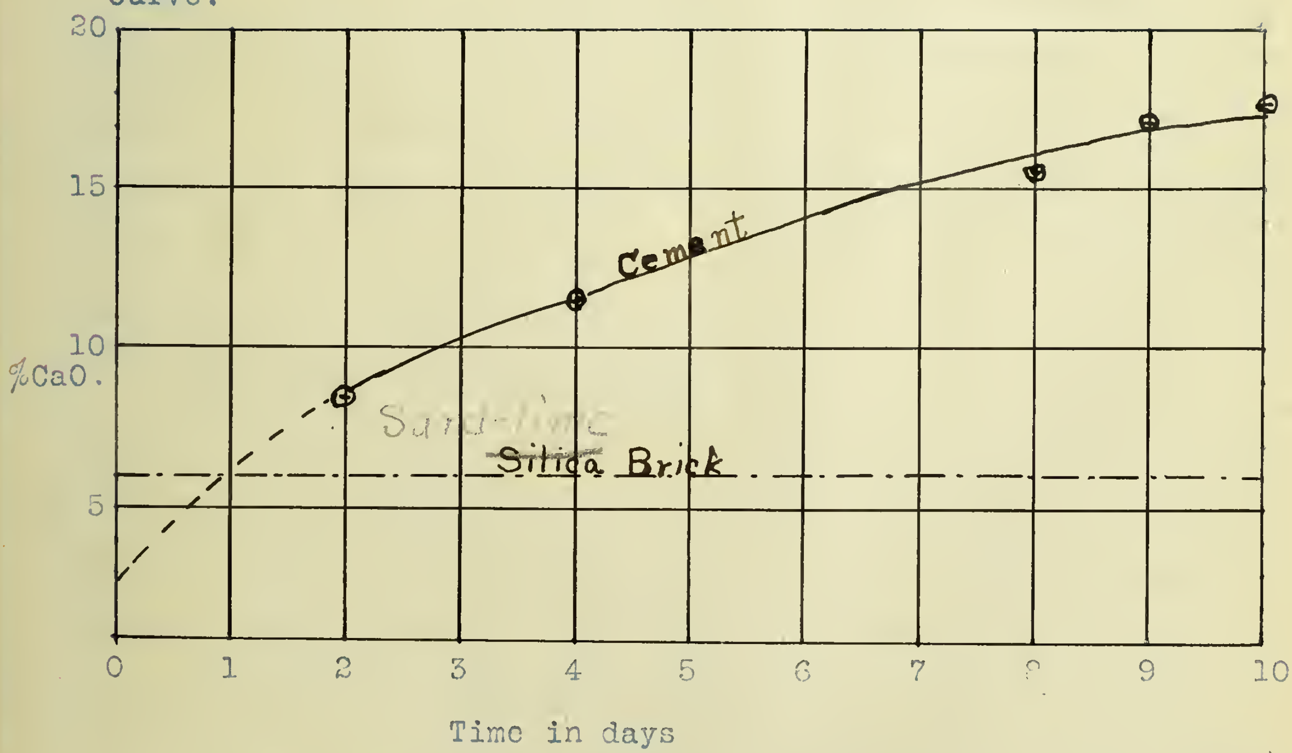
It was the object of the chemical work to study the extent of chemical combination, and to determine whether the methods available were capable of sufficient accuracy when applied to this material to admit of the determination of the empirical formula of the compound formed. The amount of free lime remaining after hardening will give an index to the extent of chemical reaction in samples made up with the same percentage of lime, as will also the per cent of combined silica. The methods used in these determinations will be described somewhat in detail.

The free lime was determined volumetrically as follows: Into a liter flask 2.8 grams of the finely divided powder were weighed and the flask filled nearly to the mark. It was allowed to stand for several days with occasional shaking, and then titrated with an N/10 solution of hydrochloric acid, after filling to the mark and allowing time to settle. If in this titration 100cc be used, then each cubic centimeter of acid used will correspond to one per cent of calcium oxide in the sample. Samples for analysis were taken so far as possible from the center of blocks, and were handled in a manner so as to avoid as far as possible a contamination from the carbon di-oxide of the air.

The results by this method were very satisfactory, duplicate determinations and those on successive days, checking to within a few hundredths of a per cent. Sugar solutions were used at first as it was thought that there might be some danger of the pure water not dissolving all the lime. A check test, however, showed that the water would dissolve several

times as much lime as was required in this determination, so the use of sugar solutions was abandoned.

It was suggested by several chemists that this method would not give accurate results owing to the hydrolyzing effect of water on the calcium silicate. These men thought that the action here would be the same as in the case of Portland cement and water. In order to test this point Portland cement was treated in the same way as sand-lime brick. By shaking vigorously every half hour for the first few hours the cement could be kept from hardening. Titrations were made at the end of the first day, and on successive days for a period of about a week. The results are shown below in the form of a curve.



These curves show conclusively that while the cement decomposes steadily giving rise to more and more free lime, the sand-lime brick is without change. After standing in contact with water for some time the cement is converted

almost wholly into a flocculent mass, which is no doubt aluminum hydroxide and silicic acid. No such effect is observed when sand-lime brick is treated with an excess of water. These experiments taken together with the fact that this material is formed in contact with water should be sufficient to show that there is no hydrolysis in the case of sand-lime brick.

In order to estimate the combined lime it was necessary to determine both total and free lime and take the difference. The total lime was also determined volumetrically, the method being as follows:-

A 250cc Erlenmeyer flask was provided with a cork through which passed a glass tube. This tube reached down into the flask to within about an inch and a half of the bottom and extended about three inches above the cork. The upper end was drawn out to a diameter of about 2 mm, and there was a hole through the side of the tube just below the cork. This arrangement provided for the escape of the steam without danger of loss of acid by spattering.

The sample was weighed into this flask and a known volume of standard acid run in. The liquid was then boiled until the acid was pretty well concentrated. It was then allowed to cool, 100 cc of water added, and the excess of acid titrated with standard alkali. Sulphuric acid was used instead of hydrochloric, as recommended by some authors, because no condenser was required, and the concentrated sulphuric acid tended to partially dehydrate the silicic acid, thus rendering it less troublesome in the titration.

The determinations by this method checked well. It will

be observed, however, that where much carbonate is present this method cannot be employed unless the per cent of carbonate be also determined, as the carbonate of lime will be estimated, in this case, as combined lime and the results will be inaccurate. No determinations of carbon di-oxide were made in this work, but precautions were taken to prevent the formation of carbonate as far as possible.

The determination of combined silica is the most difficult connected with this work. It was separated from the free silica on the principle of its solubility in dilute acids and alkali. In order to determine the extent of the solubility of the silica used, blank determinations were run. It was found that the acid used did not dissolve it appreciably, but that the 3% alkali solution in the duplicate samples took up 1.5 and 2.2% of the weight of the sample. Now with a solubility like this it is evident that very accurate work need not be expected when alkali is used for washing the residue left from the acid treatment.

In order to avoid the error inherent in the acid alkali method with such a fine-grained material as this and to determine whether concordent results could be obtained by washing with acids alone, several determinations were made. A 4% solution of HCl was employed, which was prepared by diluting the strong acid to ten times its volume. The results by this method were entirely unsatisfactory, duplicate determinations in many cases varying several per cent. The method was abandoned and subsequently all determinations were made by washing the residue left by the acid with a 3% solution of alkali carbonate. The method was the following:-

One gram of the sample was weighed into a seven inch casserole and 125cc of a 4% solution of hydrochloric acid were added. The liquid was then boiled and allowed to settle for some time. It was then filtered and washed by decantation several times with water to remove the acid. An equal volume of the alkali solution was then added and heated to near the boiling point. The liquid was decanted through a filter after settling, and the process repeated with a smaller quantity of the solution. Finaly the residue is transferred to the filter paper and the washing completed with water. The silica is then determined in the filtrate in the usual way. The results by this method, while not at all satisfactory, are very much better than those where acid alone was used.

Great difficulty was experienced in the filtration of some of the acid solutions due to a clogging of the pores of the filter- paper by the separated silicic acid. This was especially noticeable when relatively strong acids were used. By allowing time for the liquid to settle and keeping it near the boiling point the filtration was greatly facilitated.

Free silica was determined by weighing the residue left on the filter-paper, and so is subject to the same error as the combined silica. This determination was not made but a few times as it is of relatively little importance.

That these determinations are useful in giving an idea of the extent of chemical reaction, there can be no doubt, but that they can be of little value in determining a chemical formula is equally apparent.

In the first series of blocks made, the lime and silica

were mixed in the ratio to form $CaSiO_3$ and steamed for eight hours at a pressure of about 150 pounds per sq. in. The following table shows some of the determinations made.

Table No. 15

No.	~~Steam~~ Pressure	Absorption	Crushing Strength	% Free Lime	% Comb'd Lime	% Comb'd Silica	Chem H_2O
1	10000	11.9	7500	....	.....	.....	....
2	9000	12.6	....	9.45	29.00	18.55	9.77
3	5000	12.7	....	....	.....	.....	....
4	5000	....	7000	....	.....	.....	....
5	5000	....	....	6.20	31.50	21.25	11.4

It will be noticed that the sum of the combined and total lime is considerably less than the per cent of lime used in making the samples. Lest this prove confusing it may be well to say that these figures are on the sample containing both chemical and hygroscopic water, and not on the anhydrous substances as in making the mixture.

If from the results shown in the table we calculate the molecular formula (For No's. 2 & 5) on the basis of one molecule of silica, we have the following:-

No. 2, $1.67CaO \cdot SiO_2 \cdot 1.75H_2O$.

No. 5, $1.58CaO \cdot SiO_2 \cdot 1.78H_2O$.

These results though not very concordant show that there is a close relationship between the two samples.

In the next set of samples made up, three mixtures were prepared in which the percentages of lime and silica varied, and three different pressures were used on each mixture in the mould. The results are shown in the following table No. 16.

Table No. 16.

No.	8	9	10	11	12	13	14	15	16
Lime	40	40	40	50	50	50	60	60	60
Pressure lb.sq.in.	5000	10000	15000	5000	10000	15000	5000	10000	10000
Absorption	15.7	7.8	20.1	5.5	6.7	8.5	14.7	16.0	13.4
Crushing Strength	5838	6700	.....	5895	7095	6755	4145	5900	6510
Free Lime	2.00	3.05	2.80	3.25	4.75	4.80	3.45	3.35	5.00
Total Lime	24.80	25.50	27.00	28.10	38.90	30.80	37.50	39.25	29.50
Comb'd Lime	22.80	22.45	24.20	24.85	34.15	26.00	34.05	35.90	24.50
Comb'd Silica	17.68	22.70	24.60	27.90	28.10	26.07	29.47	27.74	23.00
Lime, Silica Ratio	1.29	0.99	0.98	0.89	1.24	1.00	1.15	1.29	1.05

The mean of all these lime, silica ratios is 1.09 which is very close to unity, and suggests the formula, $CaO \cdot SiO_2 \cdot xH_2O$, as the most probable for the compound. In this series of samples the water was not determined and so we put the coefficient "x" before it in the formula, but in the molecular formulae worked out from the first series of samples, it will be remembered that the number of molecules of water was practically the same as the number of lime molecules. This fact leads to the conclusion that "x" is unity, and that the formula is

$$CaO \cdot SiO_2 \cdot H_2O.$$

The above ratios are calculated from percentages of the compounds and not from molecules, but as the molecular weights of lime and silica are nearly the same this does not make a

great deal of difference. The mean value of the ratio calculated from the number of molecules is, however, 1.01 instead of 1.09.

The difficulties encountered, and the errors inherent in the method followed can readily be appreciated. In order to prove the formula it will be necessary to proceed in a somewhat different manner. During the progress of this investigation several lines of procedure have suggested themselves which promise to give results somewhat more definite than the one followed.

One of these would be to use a pure, sized quartz instead of amorphous silica. This should be of such a size that it will pass an 80 mesh screen but be retained upon a 100 mesh. If this be first boiled in acid and then alkali before making into brick it is safe to assume that there will be no silica pass into solution except that which was in combination with lime. Then by carefully excluding carbon di-oxide and using a pure lime very accurate results should be attainable.

A second method of attack would be to blend thoroughly several grams of precipitated silica with about three times its weight of pure lime, and heat for some time under high steam pressure. The large excess of lime will without doubt take into combination practically all the finely divided silica. The free lime can then be determined, as in this work or it may be completely removed by shaking with water and; decanting a sufficient number of times, and the pure compound obtained. By a similar process of washing,any calcium carbonate that may have formed during the time may be removed. The only modification necessary will be the substitution of water

saturated with carbon di-oxide for pure water.

Another piece of work which seems promising is the determination of the vapor pressure curve of the thoroughly dried material.This will no doubt add greatly to our knowledge of the chemistry of this compound, or at least give us a better idea as to whether or not a definite compound really is formed under these conditions. It should also give some valuble data concerning the water of the compound.

PHYSICAL PROPERTIES OF SOME OF THE LIME, SILICA TEST BLOCKS

The crushing strength of some of the test blocks made has already been observed in the tables in the preceding section of this work. Of the first five blocks made two were crushed, the strength comparing favorably with that of ordinary building brick. In table No. 16 it will be observed that eight blocks were broken, the highest strength being found in those containing 50 % lime and made at a pressure of 10000 lbs. per sq. in. The pressures higher than this seemed to give a poorer brick as shown by a falling off in the crushing strength and percentage of combined lime, and silica.

The per cent of water absorbed as shown in table No. 2 is rather interesting. One would expect that it would vary inversely as the pressure applied in the mould, or that it would bear some definite relation to the lime content, but no such relation is observed. From these considerations we are led to the conclusion that the best proportions for brick of this material are equal parts of lime and silica.

The appearance of these blocks was very much like that of hardened Plaster of Paris. It could be broken only with

a sharp blow from the hammer. The fracture was conchoidal. and the broken surface showed a vitreous lustre. No attempt was made to use colors as the samples were intended for chemical analysis. A fire test was made by placing one of the large blocks containing 50% of lime in a muffle furnace. It cracked into several pieces owing to a too sudden heating, but the pieces came out of the furnace without any further breaking down. Upon examination, however, the pieces were found to be full of small cracks, between which the material appeared perfectly sound. The powdered material colored a solution of phenolphthaleīn instantly showing that there was much free lime. The temperature in this test was almost a white heat.

THE USES OF ILLINOIS SILICA, (PART THE THIRD).

Some of the uses to which this fine-grained silica is already put, have been mentioned in the introduction and need not be repeated here. The study of the sand-lime brick process has shown the need for ground sand or fine-grained silica of some sort. This should open up a large field for the material, provided there are plants making this brick within shipping distance of the deposits. The use of a part of this silica will furnish an abundance of fine material, thus facilitating the hardening process, and lessening the loss due to breakage of the green brick. Ground sand may take the place of this fine silica, but it must be remembered that the grinding process is an expensive one, especially where the material to be reduced is as hard as sand and must be made very fine.

In order to test the value of this silica in sand-lime

brick several blocks were pressed using the round-grained sand mentioned above, with 10% of lime. A parallel series was prepared using the same mixture, but with 10% of amorphous silica added. The sharp-grained sand was used in a similar manner.

With the mixture first mentioned great difficulty was experienced in getting the blocks whole from the mould, and they all went to pieces in the hardening cylinder. Those in which the fine silica was used gave good blocks with crushing strength and absorption as shown below.

Table No. 17

Kind of Sample	Absorption	Crushing Strength
Round Grained Sand	10.6	1290 lbs.
Sharp Grained Sand	10.5	4500 lbs.

Other possible uses for this material are to be found in the cement industry. It is a well known fact that many clays otherwise suitable have too low a silica alumina ratio so that if they are to be used at all silica in some form must be added. This is usually done by grinding flint and putting in the right amount. Now in order to be of much value the flint must be reduced to an impalpable powder, and to do this grinding cement companies anually spend thousands of dollars. The value of amorphous silica suggests itself to any one familiar with the manufacture of cement.

Again, this material blended properly with a cheap grade of kaolin and pure limestone will no doubt lend itself admirably to the manufacture of a white Portland cement, a commodity much sought for at the present time.

It was noticed that this material when properly moistened

and blended with an equal part of lime possessed good plasticity. This fact led to some experiments along a different line. Equal parts of silica and slaked lime were mixed with enough water to render it plastic. Blocks were then prepared and allowed to dry for a short time. They were then steamed for the usual time. The blocks prepared in this way showed considerable shrinkage upon drying owing to the high content of lime, but no change was observed in the hardening cylinder. The material resembled the pressed brick that were made from the same proportions very much.

It seems probable that this method could be employed in the manufacture of decorative building material of the nature of terra cotta to advantage. No tests were made on this material. This appears to be a promising field and should be investigated further.

Blocks were also made in which one half of the above mixture was used with an equal weight of a one to three cement mixture. After an initial set some of the blocks were steamed. About a week was allowed and then they were pulled, together with some blocks of the cement mixture alone. The results are shown below.

Cement Mixture	80 lbs.
Same Steamed	140 "
Silica, Lime, Cement Mixture	210 "
Same Steamed	215 "

The blocks in which the cement was used showed no shrinkage on setting.

Another industry to which these silica deposits should

prove valuable, is the silica brick industry. Silica brick are made by mixing sand or silica with about four per cent of lime and heating to a high temperature, after shaping in a dry press. For certain purposes a very fine texture is necessary in order that the brick may be able to resist the action of slags.Fine silica is needed,then, by the manufacturer in the manufacture of these bricks.

Several attempts were made to prepare some of these brick from amorphous silica, but no attempts were entirely successful owing to insufficient temperatures being used.

SUMMARY

(1) The manufacture of sand-lime brick is now an established industry, with all the details of manufacture carefully worked out on a scientific basis.

(2) The extent of the reaction between the silica(SiO_2) and lime is in direct proportion to the surface factor of the silica.

(3) The degree of fineness of the silica may be carried to a point where the reaction with lime takes place to so great an extent as to govern the character of the product, which may be made to consist of from 80 to 85 per cent of this artificial silicate.

(4) The extent to which an artificial silicate may be formed with lime and finely divided silica suggests: (a) Its use as a bonding material with sand,giving to sand-lime brick, when thus made, a superior strength and texture. (b) The adaptability of the product for decorative material such as tile, terra cotta, etc. (c) Compounding with cement or cement mater-

ial for yielding a product having special properties of color, texture, etc.

(5) The unique character of the Illinois deposits of silica, especially considering the very finely divided condition in which it occurs, emphasizes the importance of this material and the industrial bearing it may have in extending the manufacture of products intended for building and decorative purposes.

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